

E-ISSN: 2476-6283



Journal homepage: https://arww.razi.ac.ir

# Ultrasound-assisted adsorption of Cr (VI) ions from aqueous solution: Experimental study and CFD simulation

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Adsorption of Cr (VI) ions by activated carbon nanoparticles in a sono-container

# GRAPHICAL ABSTRACT



# **ARTICLE INFO**

Article history: Received 18 February 2021 Reviewed 28 April 2021 Received in revised form 30 May 2021 Accepted 2 June 2021 Available online 5 June 2021

# Keywords:

Adsorption Ultrasound CFD modeling Bentonite Nanoparticles Activated carbon Sono-container

Article type: Research Article



# 1. Introduction

By the growth of industries, waste material deriving from industrial activities are increasing significantly. Heavy metals are one of the major pollutants entering the environment through industrial proceedings. Chromium (Cr (VI)) as one of the most toxic metals is characterized as <sup>\*</sup>Corresponding author Email: n.azimi@iauksh.ac.ir

a group of human carcinogens agents by the United States Environmental Protection Agency. Cr (VI) species have strong oxidizing properties and are highly soluble, mobile, and toxic. For this purpose, strict and precise instructions have been situated for the discharge of Cr (VI) into surface waters, and most countries have reported its permissible limit of 0.05 mg (Kakavandi et al. 2014; Makeswari et al.

How to cite: N. Niknezhad, N. Azimi, S. Ahmadi, Ultrasound-assisted adsorption of Cr (VI) ions from aqueous solution: Experimental study and CFD simulation, *Journal of Applied Research in Water and Wastewater*, 8 (1), 2021, 41-49.

# ABSTRACT

The purpose of this study was numerical and experimental investigations on the influence of ultrasound on Cr (VI) removal from aqueous solution by adsorption onto activated carbon nanoparticles. The effect of key factors on Cr (VI) elimination like media pH, absorbent mass, initial concentration of Cr (VI) and the location of ultrasound transducers were considered. To perform CFD modeling of ultrasound propagation, the vibrations of 1.7 MHz piezoelectric transducers (PZTs) were defined based on the dynamic mesh model. The experimental results indicated that by pH raising from 2 to 8, Cr (VI) removal efficiency had a decreasing trend and at pH=8, it had the lowest value. The adsorption rate increased by augmentation in the adsorbent mass (AM) due to the enhancing its specific surface area. In comparison with using a shaker, ultrasound showed lower needed contact time for Cr (VI) elimination at identical conditions. In addition, CFD results depicted that the acoustic streams were induced in the direction of ultrasound propagation, which is caused to reach the better mixing and Cr (VI) removal efficiency. Finally, the experimental data were adopted with the Langmuir and Freundlich isotherms. The comparison of these models showed that both models were well suited to experimental findings and the data compatibility with Langmuir model was greater. 2014; Mu et al. 2015; Michailides et al. 2015). However, redundant use of plating industries, electric, leather, nuclear power plants, textile industries and etc from chromates and dicorates leads to an increase in this metal in aqueous environments (Makeswari et al. 2014). Different techniques are suggested for the elimination of Cr (VI) ions from liquid solutions like chemical separation, purification, membrane separation, electro-chemical refining, ion exchange, chemical precipitation, ion exchange, and reverse osmosis can be mentioned (Selvi et al. 2015; Jing et al. 2011; Zhou et al. 2015; Jiang et al. 2013).

These techniques chiefly have failures and restrictions for examples low efficiency, high-energy demand, the necessity for specific chemicals, producing large quantities of sludge and problems of residue disposal with contaminants (Sugashini et al. 2015). Adsorption is a valuable technique of separation procedure in many natural, physical, biological, and chemical industries because of the high capability of solid substances to attract the molecules of gases or solutions. In recent years, the adsorption process has been utilized as one of the best approaches for the elimination of metal ions, which is preferred to other methods due to its easiness and low costs (Jamshidi et al. 2016). However, the adsorption process occupies a low mass transfer rate, trouble in the regeneration of adsorbent and restrictions for development and application.

To overcome this weakness, some modifications to the conventional adsorption process have been extensively investigated. Ultrasonic represent an innovative green technology that can intensify the chemical and the mass transfer processes and break the bonded between adsorbate and the adsorbent (Rahimi et al. 2014, Rahimi et al. 2015, Mansouri Jalilian et al. 2019). These consequences are due to the phenomena of shock waves, acoustic cavitation, and microstreaming. Shock waves cause to induce the microscopic agitation within interfacial films adjacent to solid particles. Acoustic cavitation is the establishment, growth, and collapse of micro-scale bubbles generated by the propagation of ultrasonic waves into a liquid medium. Acoustic micro-streaming produced by the ultrasonic waves is the basis movement of the liquid (Asfaram et al. 2016, Azimi et al. 2019, Rahimi et al. 2013). These phenomena originated from applying ultrasonic power into the adsorption process, results in an increase in the rate of mass transfer near the surface of the absorbent. In addition, when nanoparticles used as absorbent for the adsorption of metal ions, propagation of ultrasonic into aqueous solution can separate the agglomeration of nanoparticles into a permanent and homogeneous suspension because it has high energy density. Furthermore, ultrasonic works similar to an agitator or an exciter and can apply the vigorous mechanical forces in the solution, so; it can intensify the mass transfer rate in solid-liquid interphases (Mondragon et al. 2012, Zou et al. 2012). For example, Schueller and Yang considered the influence of ultrasonic on the adsorption and desorption of phenol using activated carbon and polymeric resin. They declared that for the adsorption process in a batch absorber, ultrasonic play a mixer and enhance the mass-transfer coefficient owing to the generation of cavitation and acoustic streaming. Entezari et al. 2006 utilized ultrasonic for the sorption of cadmium from aqueous solution and found that by employing ultrasonic, the porous and film diffusion coefficients of the absorbent are higher than its absence because ultrasonic waves strongly modify the mass transfer between two phases. Jing et al. 2011 performed an experimental work to examine the effect of 20 kHz ultrasonic on the adsorption and desorption of Cr (VI) on activated carbon and PVC-PPA resin. Their results showed that the adsorption rate onto resin increased and the equilibrium time decreased obviously under ultrasonic irradiation, but for adsorption onto activated carbon, ultrasonic only enhanced the adsorption rate. Zhou et al. 2015 evaluated the application of ultrasonic waves to improve the adsorption of chromium (VI) onto highly active nanoparticles of zero-valent iron (nZVI). They compared the efficiencies of Cr (VI) elimination by nZVI subject to ultrasonic and shaking and proved that the perceived rate constant  $(k_{\mbox{\tiny obs}})$  by ultrasonic is so higher than that of shaking. Wu et al. 2018 assessed the effect of ultrasonic on the adsorption and desorption processes of blueberry anthocyanins on macroporous resins. Their results show that ultrasonic mainly improved the adsorption procedure by increasing the surface roughness of the surface of the resin and strengthening the formation of the hydrogen bonds.

In another work, Mehrabi et al. 2017 used a novel absorbent for the ultrasonic energy-assisted adsorption of Cr (VI) ions from aqueous solution. In their study, the Langmuir, Freundlich, Tempkin analyzed the experimental data, and Dubinin-Radushkevich isotherm models and the equilibrium data fitted with good agreement in Langmuir isotherm equation. In all of these researches, it is illustrated that the mass transfer rate and adsorption process are enhanced by the presence of ultrasonic. It must to state that in these works low frequency ultrasonic waves have been utilized to increase the adsorption process and

application of the ultrasonic waves in the frequency spectrum above 1 MHz in mass transfer processes is limited in the literature. The ultrasonic waves in the range of MHz are able to generate more intense acoustic streaming which is responsible for mass transfer rate augmentation. Consequently, the aim of this investigation is to study the ultrasonic technology for Cr (VI) elimination from aqueous solution and adsorption onto activated carbon nanoparticles. In the experimental section, the effects of five independent parameters such as initial concentration of Cr (VI) ions, pH of the solution, adsorbent mass, ultrasonic time and the ultrasonic transducer locations on the adsorption qunity, equilibrium isotherms and kinetics models are analyzed. For this intricate procedure, it is serious to attain a further vision into nanoparticle motion, mixing, and Cr (VI) elimination rates that are influenced by the ultrasonic. Therefore, the present study also deals with Computational Fluid Dynamic (CFD) modeling of a cylindrical sono-container equipped with four high-frequency ultrasonic piezoelectrics (1.7 MHz).

# 2. Experimental section 2.1. Experimental setup and apparatus

The images of the sono-container and PZTs actuator operated in the present survey are showed in Fig. 1. The major structure of the sono-container, which was a cylinder, was fabricated of a U-PVC tube with a height of 17.7 cm and a diameter of 12 cm. A plexiglass cube with a dimension of 10 cm×10 cm×5 cm was inserted in the bottom of the sono-container. The volume of the sono-container was about 2 liters. In this sono-container, four piezoelectric transducers (PZT) with a diameter of 2.5 cm and a frequency of 1.7 MHz were used. So that, three PZTs are placed with an angle of 120 degrees on the body of the cylinder and one of them was located on the center of the upper plate of the plexiglass cube at the bottom of the sono-container. In this arrangement, because the PZTs were not in front of each other, it cause the created current waves not to collide directly with each other and does not have a negative effect on the performance of the PZTs.



Fig. 1. The real photograph of the experimental setup.

Four PVC keepers known as Glend were employed to fix the piezoelectric transducers on the body of the sono-container. Fig. 2 depicts the image of the piezoelectric transducer (PZT) with a frequency of 1.7 MHz and the used Glend in this study. The piezoelectric inside the Glend was placed between the two rubber gaskets to intercept fluid leakage. Because of the elasticity of the rubber gaskets, it does not prevent the vibration of the piezoelectric transducer (Azimi et al. 2019). In order to intercept fluid permeation, surrounding the Glends attached to the body of the sono-container sealed with silicone glue.



Fig. 2. The piezoelectric transducer (PZT) with the frequency of 1.7 MHz used in this study.

#### 2.2. Materials and solution preparation

In all experiments, deionized water (DW) was handled to make the processes more efficient. The nanoparticles of activated carbon (Asia-Pacific Co., Iran) were employed as adsorbent. A stock solution of Cr (VI) was prepared by dissolving Cr (VI) oxide peroxide, CrO<sub>5</sub>, in DW, and then the solution was diluted to the desired concentration for actual usage. Firstly, 50 mg of Cr (VI) oxide peroxide powder was dissolved in 1 liter of DW in a separate container (initial concentration of 50 mg/L). Subsequently, using a shaker at 150 rpm, the appropriate solution at room temperature (25 °C) was completely mixed. To determine the effect of pH, NaOH and HCI solutions with 0.1 M concentration were utilized and the pH was measured using pH meter (Eutech pH 700, Singapore). In this study, the effect of adsorbent concentration (activated carbon) on the elimination of Cr (VI) ion from the base solution was investigated. The amount of adsorbent was considered as a variable in the range of 2-20 g (2, 4, 8, 16 and 20) of activated carbon nanoparticles. To make any solution, a certain amount of adsorbent was dissolved in a solution containing Cr (VI) ions. At this stage, each solution involving Cr (VI) ions and adsorbent at four different pH values of 2, 4, 6 and 8 was investigated. By adding 0.1 M NaOH and 0.1 M HCl solutions, the solution pH was adjusted. It should be noted that the choice of the pH range with respect to the Eh-pH curves was related to the different modes of Cr (VI) ions.

#### 2.3. Experiment procedures

In this study, the experiments were carried out in two layouts: firstly, a solution containing Cr (VI) ions and the sorbent was poured into a 2-liter becher similar to a sono-container and placed on a shaker at 400 rpm for a specified period of time. Afterwards, a free carbon nanoparticle solution was studied by atomic adsorption decomposition to determine the recovery rate of Cr (VI) adsorption. In this research, an atomic adsorption device (Thermo model) was used to analyze the samples; the calibration curve was formed for the Cr (VI) ions and then proceeded to the next stages of the experiment.

Secondly, in order to investigate the effect of high-frequency ultrasonic waves on Cr (VI) adsorption, the previous experiments in the layout of using shaker, were repeated in the sono-container. 2 liters of suspension containing Cr (VI) ions and adsorbent were poured into a sono-container, ultrasonic transducers were switched on by the piezoelectric actuator, and then ultrasonic waves propagated into the solution. The solution was subjected to ultrasonic waves for a specified period. In the presence of high-frequency ultrasonic waves, the need for mixing with a mechanical stirrer will be eliminated (Karami et al. 2018). All experiments were carried out at room temperature, each experiment was repeated three times, and the average of the three obtained values was reported as the final amount of adsorbed Cr (VI) ions.

# 2.4. Experimental data processing

When the time of the adsorption is long enough, the adsorption system reaches to equilibrium state and thus the equilibrium amount adsorbed of Cr (VI) ions can be calculated by Eq. 1 (Rostami et al. 2020,Nayeri et al. 2019, Mousavi et al. 2019):

$$q_e = \frac{C_0 - C_e}{m} V \tag{1}$$

The elimination efficiency of Cr (VI) was calculated as follows (Rostami et al. 2020, Nayeri et al. 2019, Mousavi et al. 2019):

$$\operatorname{Re} \operatorname{movale} \operatorname{efficiency} = \frac{C_0 - C_e}{C_0} \times 100$$
(2)

where,  $q_e$  is the absorption capacity of Cr (VI) ions in equilibrium state,  $C_0$  and  $C_e$  are the initial and final concentration of Cr (VI) ions in solution, respectively. *V* is the volume of solution, and m is the mass of adsorbent.

# 2.5. CFD modeling

In the experimental section, maybe understanding the motion of solid nanoparticles, adsorption performance, and velocity distribution under the impact of acoustic streaming and micro-jets induced by ultrasonic is limited. So, to resolve this problem, computational fluid dynamic (CFD) modeling was performed by FLUENT 6.3 software to recognize this issue. There is not any exact formulated theory that has the ability to wisely prediction of the nanofluid behavior by considering it as a multi-component material. Due to such an extremely reduced dimension (smaller than 100 nm), it has been proposed that

nanoparticles can easily fluidized and hence can be evaluated very like a uniform liquid. In addition, by supposing a trivial motion between the nanoparticles and liquid, the nanofluid may be thought out like a normal single-liquid phase with potent physical properties as a function of the properties of both materials and their relative concentrations. Therefore, equations of mass, momentum, and energy are as well known for single-phase fluids that can used for nanofluids. In the present survey, the 'single-phase' method is adopted to studying the hydrodynamic of the nanofluid subjected to ultrasonic. The transport equation is described as follow (Valeh-e-Sheyda et al. 2018):

$$\frac{\partial(\rho)}{\partial t} + \nabla . (\rho \vec{\nu}) = \nabla . \vec{\tau} + S_{\phi}$$
(3)

where,  $\rho$  is the density,  $\vec{v}$  is the phase velocity,  $\bar{\bar{\tau}}$  is the diffusion term, and  $S_{\varphi}$  is the source term. The momentum balance (Valeh-e-Sheyda et al. 2018) gives:

$$\frac{\partial(\rho \vec{v})}{\partial t} + \nabla .(\rho \vec{v}^{2}) = -\nabla p + \nabla . \vec{\tau} + \rho \vec{g}$$
(4)

where, p is the static pressure and  $\rho \vec{g}$  is the gravitational body force. Stress tensor is given by (Valeh-e-Sheyda et al. 2018):

$$\vec{\tau} = \mu \left[ \nabla \vec{v} + \nabla \vec{v} - \frac{2}{3} \nabla \vec{v} \mathbf{I} \right]$$
 (5)

where,  $\mu$  is the molecular viscosity, *I* is the unit tensor, and the second term on the right hand side is the effect of volume dilation.

### 2.5.1. Geometry and grid generation

The 3-D geometry of the sono-container is presented in Fig.3. The computational area consisted of a vertical cylinder is meshed by GAMBIT 2.4 software. The type of used meshing is structured hexahedral cells. To do a more accurate meshing, the PZT faces are meshed by the triangular cells with the small sizes.

#### 2.5.2. Initial and boundary conditions

The boundary conditions are explained as follows: the wall boundary condition for the surface of PZTs and all other boundaries. The comprehensive explanations for the boundary conditions are gathered in Table 1.

Table 1. Defined boundary conditions in the model.



Fig. 3. (a) 3-D geometry of the sono-container, (b) The computational

# domain of the sono-container.

# 2.5.3. Grid dependency

In order to ensure the independence of the solution from the grid sizes, five grid sizes  $(6.4 \times 10^5, 1.23 \times 10^6, 1.54 \times 10^6, 1.78 \times 10^6$  and  $1.82 \times 10^6$  control volume numbers) of the computational domain have been investigated. The calculated velocity at a particular point of the sono-container was examined as a criterion to consider the independence of the model from the grid sizes. There was no significant change in the predicted velocity for a number of control volumes more than  $1.780 \times 10^6$ . Therefore, in order to reduce the computation time, this layout was chosen for all cases.

# 2.5.4. CFD modeling tactics

In this survey, for modeling the vibration on the PZT's surfaces, dynamic mesh model was utilized. Due to the activation of the mass transport model, the boundary condition of the velocity inlet is not appropriate for PZTs' surface. In order to represent the time-dependent equation of PZT's vibration, a user-defined subroutine (UDF) according to Eq. 1 is connected to the main program.

$$\xi(t) = \omega A_0 \sin(\omega t) \cos(2\pi \chi/\lambda)$$
(6)

where, *t* is time,  $\omega$  angular frequency  $(2\pi f)$ , *x* is the coordinate that is perpendicular to PZT surface and  $A_0$  is the maximum displacement of transducer surface (Abolhasani et al., 2012). Micro-jets and acoustic cavitation induced by propagation of high-frequency ultrasonic waves can produce macro-scale and convective flow forward with the cavitation bubbles, which causes significant velocity gradients. Then, in the present study, the RNG k- $\epsilon$  model was applied. The constants of the RNG k- $\epsilon$  model were C<sub>µ</sub>, C<sub>1- $\epsilon$ </sub>, C<sub>2- $\epsilon$ </sub> were set at 0.0845, 1.42, 1.68 and 0.85, respectively. The SIMPLE algorithm was used for pressure-velocity coupling and the unsteady-state condition was specified for the solver. The time step must be smaller than the time period of the ultrasonic wave. Therefore, in this modeling, the time step of this unsteady-state procedure was put at one-eighth the period of 1.7 MHz ultrasonic wave equal to 7.353×10<sup>-8</sup>s. The momentum, turbulent kinetic energy, and turbulent dissipation rate were discretized by the second-order upwind scheme.

# 3. Results and discussion

# 3.1. Influence of pH on the adsorption of Cr (VI) ions

The pH is a key factor in the absorbing of heavy metal ions from solutions. Therefore, pH dependence was investigated for the elimination of Cr (VI) ions at a constant contact time in both cases layouts of the shaker and ultrasonic waves. Fig. 4 shows the percentage removal of Cr (VI) ions from the solution using a shaker and a sono-container at a temperature of 25 °C, adsorbent mass (m) of 2g and the different contact times. At this stage, all PZTs on the body of the sono-container is switched on and the ultrasonic waves are propagated into the sono-container. As shown in this figure, for both layouts of the use of shaker and the sono-container, a reduction of the efficiency of Cr (VI) elimination has decreased from 2 to 8, and at pH 8 it has the lowest amount of Cr (VI) elimination. pH is one of the most important parameters for controlling of the adsorption process of metal ions. Cr (VI) is present in aqueous solutions in the forms of CrO4-, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, HCrO<sup>4-</sup> and H<sub>2</sub>CrO<sub>4</sub>, and the oxidation states of these forms depend on the pH of the environment. At pH=2, the chromium in the solution is more  $Cr_2O_7^{2-}$  and  $HCrO^{4-}$ . In addition, at this pH, the amount of H<sup>+</sup> on the surface of the activated carbon increases. As a result, due to the difference in loads generated between chromium states and adsorbent levels, electrostatic gravity is generated, which improves the adsorption process. At higher pHs, the amount of adsorption decreases due to competition between  $CrO_4^{2^\circ}$  and OH on the adsorbent surface. The comparison between Fig. 4 a and Fig. 4 b shows that with increasing the contact time from 20 min to 40 min, the amount of Cr (VI) elimination in the shaker increased, while it decreased in the case of using the sono-container. Therefore, the contact time is an important parameter and it should be further investigated. In the next section, the effect of this parameter will be evaluated further.

# 3.2. Effect of contact time on the adsorption of Cr (VI) ions

Fig. 5 shows the time-dependent elimination behavior of Cr (VI) ions from aqueous solution using activated carbon adsorbent. As shown, for both layouts, the amount of Cr (VI) elimination increases with increasing the contact time and the equilibrium time from 2 to 15 min. However, with regard to the use of the shaker, the elimination rate of Cr

(VI) from the contact time between 15 min and 50 min is still increasing and in 50 and 60 min, the percentage of elimination is equal. In fact, the percentage of Cr (VI) elimination in a shaker has reached its maximum value of 80 %, within 50 min.



Fig. 4. Removal efficiency of Cr (VI) using shaker and sono-container at T=25°C and m=2 g. (a) t=20 min, (b) t=40 min.

The initial adsorption rate is very fast to adsorb Cr (VI) due to a large number of sites on the nanoparticles. According to the results obtained for using the shaker, the contact time of 50 min is chosen as the most effective contact time to remove Cr (VI). However, as shown in Fig. 5, in the case of the sono-container, the elimination rate of Cr (VI) is very fast in the first 15-20 min, and its maximum value at a contact time of 15 min reached to 82 %, and after that, the elimination rate of Cr (VI) has been decreasing. In fact, the adsorbent surface and its sites initially increased by ultrasonic adsorption in the solution and hence, the adsorption rate of Cr (VI) is high by adsorbent, while after 15 min, apparently due to the evaporation of ions from the adsorbent surface, the disposal process has occurred and even Cr (VI) has been transferred from the surface of the nanoparticles to the aqueous solution. This means that high-frequency ultrasonic waves can produce high percentages of elimination of Cr (VI) from aqueous solution, due to the creation of micro-screams and acoustic cavitation phenomena. The application of ultrasonic waves into the sono-container increases the adsorption rate over a short period using a small amount of adsorbent material. Ultrasonic through secondary activities such as cavitation (nucleation, growth, and temporary collapse of small gas bubbles) increases the mass transfer through the physical phenomena such as micro-streams, micro-turbulences, acoustic waves (or shock), and micro-jets. This phenomenon occurred without significantly altering the equilibrium properties of the absorption/desorption system. According to the results obtained for using the sono-container, the contact time of 15 min is selected as the most effective contact time for the elimination of Cr (VI) under the influence of high-frequency ultrasonic waves.



Fig. 5. Effect of contact time on the removal efficiency of Cr (VI) using shaker and sono-container at T=25°C, m=2 g and pH=2.

### 3.3. Effect of adsorbent mass on the adsorption of Cr (VI) ions

In order to investigate the effect of adsorbent mass on the chromium absorption process, four other values for adsorbent containing 4, 8, 16 and 20 g of activated carbon nanoparticles in 2 liters of Cr (VI) solution are tested. Fig. 6 shows the effect of adsorbent mass on the amount of elimination of Cr (VI) from aqueous solution for both layouts of the use of shaker and sono-container.



Fig. 6. Effect of absorbent mass on the removal efficiency of Cr (VI) using shaker and sono-container at T=25 °C and pH=2.

Based on Fig. 6, the adsorption rate of Cr (VI) in the high amount of adsorbent (2 g to 16 g) increased due to increasing its surface area. The highest elimination percentages of Cr (VI) for using shaker and sono-container were 83 %, and 85.4 %, with the contact times of 50 min and 15 min, respectively. Increasing the specific area and the availability of more active adsorbent sites in a higher amount of adsorbent is associated with an increase in adsorption rate from 2 g to 16 g. In both cases, the efficient amount of adsorbent was 16 g and no significant increase was observed with increasing adsorbent dose of more than 16 g for Cr (VI) elimination. Maybe in the case of using shaker exceeding the adsorption rate from a 16 g leads to agglomeration of particles consequently leads to a reduction in their surface area. For using sono-container, propagation of ultrasonic into aqueous solution can separate the agglomeration of nanoparticles into a permanent and homogeneous suspension because it has high energy density. Furthermore, ultrasonic works similar to an agitator or an exciter and can apply the vigorous mechanical forces in the solution, so; agglomeration of nanoparticles could be reached to minimum state. However, for the adsorption dose higher than 16 g, a very small change was observed in removal efficiency of Cr (VI) and it remains nearly constant, 16 g was selected as optional value of adsorbent dose thus more increase in it have no noticeable effect on the removal efficiency. Considering that in all of the above experiments, the sono-container with a shorter contact time compared to the shaker, performed better in removing Cr (VI) ions from aqueous solution, so in the next experiments, the sono-container is used.

# 3.4. Investigation the effect of PZTs locations on the adsorption of Cr (VI) ions

In this section, the effect of the position of PZTs on the elimination of Cr (VI) from the aqueous solution at pH = 2 and m = 16 g was investigated in five states: 1. A piezoelectric transducer on the body of the sono-container was activated (Case1). 2. Two piezoelectric transducers on the body of the sono-container were activated (Case 2). 3. All three piezoelectric transducers on the body of the sono-container were activated (Case 3). 4. Only the piezoelectric transducer on the bottom plate of sono-container was activated (Case 4). 5. All of the piezoelectric transducers on the body of the sono-container were activated (Case 5). Table 2 shows the results of the study on the effect of the position of PZTs on the elimination of Cr (VI) ions from the aqueous solution. The results show that the activation of all PZTs has the best performance for removing Cr (VI). Nevertheless, the results of the activation of the bottom PZT have also been close to the performance of the activation of all PZTs. This is due to the ability of bottom PZT to create micro-streams, and therefore dispersion and throwing of nanoparticles in the aqueous solutions that prevent their sedimentation and increase the special adsorbent surface due to acoustic cavitation and the development of jet micro-jets. This effect has been greater in the event that all PZTs are switched on. According to this table, when a PZT is active, the lowest percentage of Cr (VI) elimination was observed, which is probably because the ultrasonic waves emitted from a PZT had not a high ability to induce mixing and mass transfer. After cases 4 and 5, case 3 states that the activation of all three PZTs has a better performance than the two cases of activation of one and two PZT ones. In general, it can be said that high-frequency ultrasonic streams have a high ability to disperse the nanoparticles inside the solution, and also the collision of fluid jets with them, causing more rotational forces and at a smaller scale near the nanoparticle surface, and therefore the mixing process and the adsorption of Cr (VI) elimination on the adsorbent surface have intensified.

Table 2. Effect of PZT locations on the removal efficiency of Cr (	VI)
from aqueous solution, $pH=2$ , $m=16$ g and $T=25$ °c.	

Case of activated PZT	Removal efficiency, %	
Case 1	72.2	
Case 2	84	
Case 3	80.5	
Case 4	84	
Case 5	85.2	

3.5. Effect of initial concentration of Cr (VI) ions on the adsorption process

The effect of initial chromium concentration is another parameter that was studied for the elimination of Cr (VI) by activated carbon powder. In all experiments of before sections, the initial concentration of Cr (VI) was  $C_0 = 0.05$  g/L. In this case, three concentrations including  $C_o = 0.025$  g/L,  $C_o = 0.1$  g/L and  $C_o = 0.015$  g/L were investigated. Fig. 7 shows the effect of the initial concentration of Cr (VI) ions in the aqueous solution on its percentage elimination at m=16 g and pH=2 while all PZTs were activated. From Fig. 7, it can be concluded that there is a high dependence between the elimination efficiency and the initial concentration of Cr (VI) ions. So, by increasing the initial concentration, the available absorbent sites are reduced and, as a result, the elimination efficiency decreases. Since in the low concentration, available sites to the adsorbent surface are greater. As shown in Fig. 7, by an increase in the concentration of Cr (VI) ions from 0.225 to 0.05 g/L, the percentage of Cr (VI) ions decrease from 87 % to 85 %, respectively. While by increasing Co from 0.05 to 0.15 and 0.15 g/L, the percentage of Cr (VI) ions has a decreasing trend, which is due to the reduction of the adsorption capacity of Cr (VI) by nanoparticles and filling their capacity. By increasing the initial concentration of Cr (VI) in the solution, the elimination efficiency is reduced. Increasing the

initial concentration of Cr (VI) causes less adsorbed sites to adsorb more chromium in the solution. Therefore, the adsorbent in lower initial concentration has better adsorption properties.



Fig. 7. Effect of initial concentration of Cr (VI) on its removal efficiency using sono-container at T=25°C, m=16 g and pH=2.

#### 3.6. Adsorption isotherms

The adsorption of Cr (VI) significantly is affected by the initial concentration of Cr (VI) ions in the aqueous solution. In this section, the initial concentration of Cr (VI) varied from 25 to 150 mg/L, while the adsorbent mass was 16 g/L, pH=2, and the contact time was 15 minute for use of the sono-container. Experimental data were adapted to Langmuir and Freundlich isotherm models. Langmuir isotherm model was used to describe the chemical composition and coating of an absorber layer on the nanoparticles, and its linear form can be expressed by the following equation (Sayadi et al. 2016):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{7}$$

where,  $q_e$  is the amount of Cr (VI) absorbed in equilibrium state in mg/g, Ce is equal to the concentration of Cr (VI) in the solution in mg/L,  $q_{max}$  and  $K_L$  are the Langmuir constants, indicating the adsorbent saturation capacity and the energy term.



Fig. 8. Data fitting by Langmuir adsorption model using sonocontainer at T=25°C, m=16 g and pH=2.

By data fitting with the Langmuir model, as shown in Fig. 8,  $1/q_m$  is equal to 6/36, that means  $q_m = 0.0273$  g/L and  $K_L = 33.3$  L/g. The Freundlich isotherm model illustrates the distribution of active and energy sites and heterogeneous adsorbent surfaces by the following equation (Sayadi et al. 2016):

$$q_e = K_f C_e^{1/n} \tag{8}$$

where,  $K_f$  and 1/n are Freundlich constants related to absorption capacity and absorption intensity. As indicated in Fig. 9, in the Freundlich model, the value of n is equal to 1.36 and  $K_f$ =0.188. The comparison between these two models shows that both models are well fitted with experimental data, and of course, the value of R<sup>2</sup> is higher in the Langmuir model, therefore the data compatibility with this model is greater.



Fig. 9. Data fitting by Freundlich adsorption model using sonocontainer at T=25°C, m=16 g and pH=2.

# 3.7. CFD results

For the purpose of the flow pattern evaluation, Fig. 10 exhibits the velocity vectors into the sono-container at a horizontal slice (Y=0) after the activation of all PZTs. This figure shows created flow toward the ultrasonic transmission after PZTs activation.

By considering Figs. 10 and 11 it can be observed the activation of all three beside PZTs causes horizontal streams inside the sonocontainer, which are perpendicular to the stream generated by bottom PZT. Also Fig. 11 shows that acoustic streams due to the bottom PZT and besides PZTs can affect the fluid behavior through the sonocontainer, which pushes the fluid in four directions inside the sonocontainer. Thereby, Fig. 11 demonstrates that when the micro-particles are in sono-container, extra fluid flows are seen because of fluid and micro-particles interaction. The velocity contours at different positions along the sono-container length (Y-axis) are compared in Fig. 12.



Fig. 10. Velocity vectors at a horizontal slice (Y=0) after activation of all PZTs.



Fig. 11. Velocity vectors with activation of all PZTs at three slices Y = 0, Z=0 and X=0.





Comparisons are made between the velocity magnitude at the surfaces located below the three-beside PZTs and the surfaces located upside the three-beside PZTs and also near the bottom PZT. In this figure, Y is the distance from the centerline of sono-container and threebeside PZT surfaces. From Fig. 12 a, it can be deduced that at the high distance from the surface of PZTs (Y = 0.07), the velocity values inside the sono-container is very low and close to 0.0002 m/s. According to Fig. 12, at the centerline-horizontal surface of the sono-container and crossing the three-beside PZTs (c) and near the surface of bottom PZT (e), higher values of velocity can be seen compared to upper and lower surfaces of Y=0 (Y=0.03, 0.07, -0.03), which are results of ultrasonic broadcast from the surface of these PZTs. In addition, Fig. 13 shows that by enhancing spacing from the PZTs surface, the velocity magnitudes are decreased. Generally, Fig.13 illustrates the highest velocity values are related to the surface of active PZTs and ultrasonic wave propagation causes to increase in the velocity magnitude within the sono-container.

#### 3.8. Validation of CFD results

The velocity magnitudes induced by propagation of 1.7 MHz ultrasound into the sono-container was validated by velocity measurements at the different distance from the bottom PZT. According to experiences of authors' research team, hotwire method was used to measure velocity magnitudes inside the sono-container by the equipment that used in Abolhasani et al. (2012). In order to ensure the accuracy of the approach, CFD results of the velocity magnitudes at five distances from the bottom PZT in the sono-container were compared by experimental data. An absolute relative error (ARE (%)) was calculated using the following formula:

$$ARE(\%) = \frac{Experimental velocity-Numerical velocity}{Experimental velocity} \times 100$$
(9)

The results of Table 3 shows that the maximum error obtained are 4.188 %, which indicates the high accuracy of the CFD model.



Fig. 13. Velocity contours with activation of all PZTs at three slices Y = 0, Z=0 and X=0.

Table 3. Comparison between the CFD-predicted velocity and				
measured velocity.				

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Distance from the bottom PZT, cm	Experimental velocity, m/s	Numerical velocity, m/s	Error, %		
0	0.00146	0.00152	4. 101		
1	0.001265	0.001302	2.921		
2	0.000843	0.000838	0.593		
3	0.000573	0.000549	4.188		
4	0.000423	0.000407	3.782		
5	0.000251	0.000247	1.593		

Fig. 14 shows the contour of absolute pressure (Pa) with activation of all PZTs at three slices Y = 0, Z=0 and X=0. Obviously, the fluid at the bottom of the sono-container has the highest pressure. The pressure difference from top to the bottom of the container is mainly due to hydrostatic. Although, the piezoelectric transducers periodically induce ultrasound waves in the liquid and therefore, it causes to alterations in velocity and pressure simultaneously. These pressure changes begin to spread throughout the liquid exactly from the bottom PZT. Each PZT puts such pressure on the liquid in the direction of vibration, so the pressure changes will definitely vary along the height because there is also a PZT at the bottom of the container. This phenomenon is well illustrated in Fig. 14. However, the effect of PZTs on the pressure difference from top to the bottom of the sono-container is negligible compared to hydrostatic pressure.



Fig. 14. Contour of absolute pressure (Pa) with activation of all PZTs at three slices Y = 0, Z=0 and X=0.

# 4. Conclusions

Experimental and numerical studies of using high frequency ultrasonic to intensify Cr (VI) elimination from aqueous solution by adsorption onto activated carbon nanoparticles have been performed. Ultrasonic transducers were located on the body of a cylindrical container and introduce 1.7 MHz ultrasonic into the aqueous solution.

The experimental results of Cr (VI) elimination efficiency and mass transfer characteristics of using ultrasonic were compared with those of shaking. The influences of five independent parameters such as pH. absorbent mass, initial concentration of Cr (VI), sonication time and the location of ultrasonic transducers on the elimination efficiency were evaluated. The experimental results depicted that by increasing pH from 2 to 8, Cr (VI) elimination efficiency decreased and pH=8 showed lowest value. By increase in the adsorbent mass (m), the absorption rate of Cr (VI) increased because of the increase in specific surface area of activated carbon nanoparticles. In identical conditions, sonication time for Cr (VI) adsorption was lower than the contact time by shaking to reach equal elimination efficiency. Indeed, the highest elimination efficiency of Cr (VI) for the shaker and the sono-container were 83 % and 85.4 %, respectively, with the contact times of 50 min and 15 min, respectively. It deduced that acoustic and micro-streams generated by high-frequency ultrasonic had the high ability to induce mixing and strong mechanical effect inside the sono-container. In addition, micro jets induced by 1.7 MHz ultrasonic collided with the surface of nanoparticles and so the adsorption of Cr (VI) on the adsorbent was increased. The comparison of Langmuir and Freundlich isotherms showed that both investigated models were well suited to experimental data and the data compatibility with the Langmuir model was greater. In order to CFD modeling of ultrasonic propagation, the vibrations of 1.7 MHz piezoelectric transducers (PZTs) were defined based on the dynamic mesh model. CFD results depicted that the acoustic streams were generated in the direction of ultrasonic propagation, which it caused to reach the higher mixing and Cr (VI) elimination efficiency. From this study, it was found that it was possible to reach the high elimination efficiency of Cr (VI) by activated carbon nanoparticles using simultaneous sonication by high-frequency ultrasound in the little time compared to shaking time.

#### Acknowledgment

The authors would like to thank Islamic Azad University, Kermanshah Branch for providing the support to carry out this work.

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